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(54) Sealable films.

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GB-A- 2 028 168
US-A- 4 230 767
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ACTORUM AG

Description

This invention relates to films based on polypropylene including those which can be sealed by the application of heat.

Various polypropylene films have been described, e.g. in GB 2 028 168A, EP 135 178 and DE 3 247 988 where the core or substrate of the film is polypropylene. Various additives are added for example certain modulus improvers, certain antistatic media, siloxanes and pigments.

Example 10 of GB 2 028 168A uses a core layer of polypropylene admixed with 15 weight % of a polyterpene resin having a softening point of 115°C (Zonarez 7115) and a single component seal layers of a random propylene-ethylene copolymer.

US 4 230 767 discloses an improved seal packaging structure with a core layer or base layer to which lower molecular weight thermoplastic resins may be incorporated which resins may vary widely and have no specific softening points. Sealability is stated to be improved by the incorporation of a low molecular weight thermoplastic resin such as hydrocarbon resins.

The invention aims to provide a film of which the seal strength properties are improved over those previously obtained having a single component seal layer. In this way either the seal strength is improved at the same temperature or the same seal strength can be obtained at lower temperature.

According to this invention a film, particularly a sealable film comprises a base layer comprising 70 to 97 weight % preferably 70 to 90 weight % of a polyolefin and 3 to 30, preferably 10 to 30 weight % of a resin of lower molecular weight than that of the polyolefin and a softening point of from 120 to 180°C, said layer having on at least one surface thereof 1 to 20 weight % based on the weight of the base layer, of a film layer comprising a copolymer of 80 to 99 weight % of propylene and 1 to 20 weight % of ethylene.

These films are capable of being used in the packaging industry and can meet the stringent criteria which are required for such films, such as sufficiently high modulus and excellent clarity. In addition, they have good barrier properties by which we mean low permeability to water vapour and gases, particularly oxygen. The films also have superior seal strength properties and are especially useful in heat seal packaging although they are useful in other packing outlets where cellophane is traditionally used, such as twist wrapping.

The base layer comprises a polyolefin and a low molecular weight resin. The polyolefin is preferably a polymer of a mono-alpha olefin containing from 2 to 8 carbon atoms and particularly 2 to 4 carbon atoms per molecule. Thus the polymer may be a homopolymer of one of the following olefins: ethylene, propylene, butene-l and 4-methyl pentene-l, or hexene or a copolymer of two or more of these olefins. A particularly suitable material for the base layer of the film is polypropylene, especially a high molecular weight stereoregular predominantly crystalline polymer of propylene. Alternatively, a copolymer of propylene with up to 20 weight per cent of another olefin, e.g. ethylene, could be used. An especially preferred polyolefin is an isotactic polypropylene with a density of from 0.86 to 0.92 g/ml measured at 23°C according to ASTM D l505 and a melt flow index of from l to l5 g/l0 min as determined according to ASTM Dl238 (conditions 230°C and 2.l6 kg). It may be made by Ziegler polymerisation methods using for example $AlCl_3$ and $TiCl_4$ as catalyst.

The other component of the base layer is the low molecular weight resin, preferably a hydrogenated resin. This resin has a molecular weight below that of the polyolefin and is usually less than 5000, preferably less than l000, for example, 500 to l000. The resin can be a natural or synthetic resin and can have a softening point as measured by ASTM E 28 of from 120°C to 180°C, e.g. preferably up to 150°C, or up to 140°C.

Suitable resins which can subsequently be hydrogenated are hydrocarbon resins, ketone resins, polyamide resins, colophonium, coumarone resins, terpene resins, chlorinated aliphatic or aromatic hydrocarbon resins. Examples of hydrocarbon resins are polymers of coke oven gas, cracked naphtha, gasoil and terpene oil.

Particularly preferred hydrogenated resins are hydrogenated petroleum resins. These are usually prepared by catalytically hydrogenating a thermally polymerised steam cracked petroleum distillate fraction, especially a fraction having a boiling point of between 20° and 280°C. These fractions usually are of compounds having one or more unsaturated cyclic rings in the molecule, such as cyclodienes, cycloalkenes and indenes. It is also possible to hydrogenate resins produced by the catalytic polymerisation of unsaturated hydrocarbons.

Before hydrogenation occurs the polymerised resin is usually dissolved in a saturated hydrocarbon solvent such as heptane. The hydrogenation catalysts used may be nickel, reduced nickel, or molybdenum sulphide. Hydrogenation can take place in a single stage at a temperature of 200°C to 330°C, preferably from 210°C to 230°C at a pressure of 20.26 to 121.56 bar (20 to 120 atmospheres), more preferably from 30.39 to 91.17 bar (30 to 90 atmospheres) for a period of 5 to 7 hours. After filtering off the catalyst, the solvent is removed by distillation and recovered for recycling. An improved hydrogenation process leading to increased yields of high quality hydrogenated hydrocarbon resins is described and claimed in EP-A 0 082 726.

The ratio of polyolefin to the lower molecular weight resin in the base layer is 70 to 97, preferably 70 to 90 weight per cent of polyolefin and 3 to 30, preferably l0 to 30 weight percent of lower molecular weight resin. More preferably the relative amounts are respectively 75 to 85 weight per cent and 15 to 25 weight per cent, for example about 80 weight per cent and 20 weight per cent.

The base layer or core of the film has on one or preferably both surfaces 1 to 20 weight per cent, preferably 1 to 10 weight per cent and particularly about 5 weight per cent for the or each surface based on the weight of the base layer, of a copolymer of 80 to 99 weight per cent of propylene and 1 to 20 weight per cent of ethylene, such copolymers being advantageously random in nature and frequently referred to as random copolymers. This randon copolymer preferably comprises 90 to 99 weight per cent, especially 94 to 98 weight per cent, e.g. about 95.5 weight per cent of propylene, the remainder being ethylene and is especially useful to provide heat-sealability.

This random copolymer of propylene and ethylene is usually an isotactic propylene-ethylene copolymer with a density of from 0.86 to 0.92 g/cc measured at 23°C according to ASTM D 1505 and a melt flow index of from 2 to 15 g/10 min as determined according to ASTM D 1238 (conditions 230°C and 2.16 kg). It may be made by well-known polymerisation methods using a Ziegler catalyst, for example, $AlCl_3$ and $TiCl_4$.

The films of this invention, i.e. multilayer films are suitably formed by combining the components (which may if desired include other components such as an antistatic medium, blocking agents and slip aids) of the base layer and surface layer(s) in a conventional manner, preferably by a simultaneous co-extrusion technique.

Multiple-layer films according to the invention may be unorientated or uniaxially orientated, but are preferably biaxially orientated by drawing in two mutually perpendicular directions in the plane of the film to impart strength thereto. Orientation of flat film may be effected by a stenter technique, while orientated tubular film is suitably produced by coextruding the polymeric materials in the form of a multilayer tube from an annular die, cooling the extruded tube (the cast tube), reheating and inflating the tube by the so-called "bubble" process to introduce transverse orientation, and simultaneously elongating the tube longitudinally to orientate the film in a lengthwise direction. The film is then preferably "heat-set", i.e. dimensional stability of the film is improved by heating the film, while restrained against thermal strinkage, to a temperature above the glass transition temperature of the polymer from which the film is formed but below the melting point thereof.

The films may vary in thickness depending on the intended application, but films of a thickness of from 2 to 150 µm are usually suitable. Films intended for packaging are usually from 10 to 60 µm thick. The thickness of the or each outer layer is usually from 0.05 to 2.5 µm.

Example

In this Example coextruded films of different composition were made and compared as to their sealability, stiffness, optical properties and barrier properties.

These films were biaxially orientated by drawing in two materially perpendicular directions in the plane of the film to impart strength thereto. The stenter technique was used to impart an orientation ratio of 500% in machine direction and of 900% in transverse direction. Each of the biaxially orientated films had two seal layers of 1 µm thickness while the total thickness was about 22 µm.

The first film which was for comparison purposes consisted of a core of isotactic polypropylene having a density of about 0.90 g/ml measured at 23°C according to ASTM D 1505 and a melt flow index of 2.8 g/10 min as determined according to ASTM D1238 (conditions 230°C and 2.16 kg). On both faces of the core there was a surface film of a random copolymer of about 95.5 weight per cent propylene and 4.5 weight per cent of ethylene. This was an isotactic copolymer with a density of 0.90 g/ml measured at 23°C according to ASTM D 1505 and a melt flow index of 6.5 g/10 min as determined according to ADTM D1238 (conditions 230°C and 2.16 kg).

The second film was the same as the first film except that the core was a blend of 80% by weight of the isotactic polypropylene used as the core of the first film and 20% by weight of a hydrogenated petroleum resin. This resin was prepared by catalytically hydrogenating a thermally polymerised steam cracked petroleum distillate fraction having a boiling point between 20° and 280°C. The hydrogenation process was carried out as described in EP-A 0 082 726. The resulting resin was characterised by a Ring and Ball softening point of 125°C.

The accompanying Fig 1 to 7 show the results obtained for the seal strength, hot tack, haze, gloss, stiffness and barrier properties for films 1 (comparative) and 2 (according to the invention)

These tests were carried out as follows:

Seal strength

This is the "cold" heat seal strength of the film which is measured after the seal has cooled to ambient temperature and the full potential strength of the seal has developed.

A Packforsk Hot Tack Tester (model 52-B) from Design & Test Consult AB (Bromma-Sweden) has been used to make the heat seals. A strip of 15 mm wide and some 280 mm long is thereto folded over upon itself and sealed together between the heated jaws of this instrument.

The formed seal has an area of some 15 × 5 mm. Dwell conditions on the seal have been kept constant at a pressure of 5 bar and a dwell time of 0.5 seconds. To measure the seal strength, the instrument is used in a mode whereby upon opening of the sealing jaws the automatic peeling action used for hot tack measurements is not activated. The seal is instead cooled to ambient temperature. The unsealed ends of the strip are then attached to the jaws of a tensile testing machine. The force required to break the seal at a rate of 508 mm/min is recorded by the tensile tester and expressed as the seal strength in kg/15 mm.

Hot tack

This is the strength of the heat seal measured just after the seal has been made and before the thermal energy employed to form the heat seal has dissipated. The hot tack has been determined using the same Packforsk instrument. The heat seal is made as described above but just after the opening of the sealing jaws a peeling action is now automatically started and the force to break the seal is automatically recorded and expressed as the hot tack in kg/15 mm. The peeling operation takes places at a controlled delay time (= time between opening of the jaws and start of the peeling operation) and controlled peel rate. Following constant conditions have been used for all hot tack determinations : delay time = 0.9 seconds, peel rate = 100 mm/s.

Haze and gloss .

These optical properties of the film have been determined with a Gardner Hazemeter, haze according to ASTM D1003 and gloss according to ASTM D523.

E-modulus

The modulus of elasticity which is a measurement of film stiffness has been determined from the tensile test of 15 mm wide film samples according to DIN 53 457

Barrier Properties

Humidity and oxygen barrier properties were determined by measuring the water vapour transmission rate (WVTR) and the oxygen transmission rate (OTR). WVTR has been measured according to ASTM F 372 at 37.4°C and 100 % relative humidity using a Permetran W5 instrument from Modern Controls Incorporated. OTR was measured according to ASTM D 3985 at 27°C using an Oxtran Twin instrument also from Modern Controls Incorporated.

From Fig 1 it can be seen that the seal strength (kg/15 mm) for film 2 is much higher at temperatures of between 100° and 110°C and above 130°C than for film 1. Between 110° and 130°C the seal strength is comparable or higher than for film 1.

From Fig 2 it can be seen that the hot tack (kg/15 mm) for film 2 is much better than for film 1 for temperatures up to about 110°C.

From Fig 3 and Fig 4 it can be seen that there is less haze and more gloss for film 2 than with film 1.

From Fig 5 it can be seen that the stiffness of film 2, as measured by the E-modulus, is significantly higher than the stiffness of film 1.

From Fig. 6 and Fig. 7 it can be seen that the barrier properties of film 2 are about twice as good as those of film 1.

It is quite surprising that with the presence of the relatively small amount (20 weight %) of hydrogenated resin in the base layer one achieves such better results compared with the prior art film.

Claims

1. A film comprising a base layer which comprises 70 to 97 weight % of a polyolefin and 3 to 30 weight % of a resin having a molecular weight lower than that of the polyolefin, said layer having on at least one surface thereof 1 to 20 weight % based on the weight of the base layer, of a film layer consisting of a copolymer of 80 to 99 weight % of propylene and 1 to 20 weight % of ethylene, characterised in that the resin has a softening point of from 120 to 180°C.

2. A film according to claim 1 in which the base layer comprises 70 to 90 weight % of the polyolefin and 10 to 30 wt. % of the resin.

3. A film according to claim 1 or claim 2 in which the copolymer is a random copolymer.

4. A film according to any of the preceding claims wherein the polyolefin in the base layer is a polymer of a mono alpha olefin containing 2 to 4 carbon atoms per molecule, preferably polypropylene.

5. A film according to claim 4 wherein the polypropylene is an isotactic polypropylene with a density of from 0.86 to 0.92 g/ml measured at 23°C according to ASTM D 1505 and a melt flow index of from 1 to 15 g/10 min as determined according to ASTM D1238 (conditions 230°C and 2.16 kg).

6. A film according to any one of the preceding claims wherein the resin is hydrogenated.

7. A film according to claim 6 wherein the hydrogenated resin in the base layer is a hydrogenated petroleum resin.

8. A film according to claim 7 wherein the hydrogenated resin has been prepared by hydrogenating using a hydrogenation catalyst at a temperature of 200° to 330°C, a thermally polymerised steam cracked distillate fraction or a catalytically polymerised unsaturated hydrocarbon fraction.

9. A film according to any of the preceding claims in which the resin has a softening point as measured by ASTM E28 up to 150°C.

10. A film according to any one of the preceding claims wherein the base layer comprises 75 to 85 weight % of polyolefin and 15 to 25 weight % of resin.

11. A film according to any one of the preceding claims wherein the base layer has on each surface 1 to 10 weight per cent based on the weight of the base layer of said film layer consisting of said random copolymer.

12. A film according to anyone of the preceding claims wherein the copolymer is a random copolymer compring 94 to 98 weight per cent of propylene and 2 to 6 weight per cent of ethylene.

13. A film according to any one of the preceding claims wherein the random copolymer is an isotactic propylene-ethylene copolymer with a density of from 0.86 to 0.92 g/ml measured at 23°C according to ASTM D 1505 and a melt flow index of from 2 to 15 g/10 min as determined according to ASTM D1238 (conditions 230°C and 2.16 kg).

14. A film according to any one of the preceding claims which is biaxially orientated.

15. A film according to any one of the preceding claims which is 10 to 60 µm thick and wherein the thickness of the or each outer film layer is 0.05 to 2.5 µm.

Patentansprüche

1. Folie, die eine Basisschicht aufweist, die 70 bis 97 Gew.-% eines Polyolefins und 3 bis 30 Gew.-% eines Harzes mit einem niedrigeren Molekulargewicht als das Polyolefin enthält, wobei diese Schicht zumindest auf einer Oberfläche, bezogen auf das

Gewicht der Basisschicht, 1 bis 20 Gew.-% einer Folienschicht aufweist, die aus einem Copolymer aus 80 bis 99 Gew.-% Propylen und 1 bis 20 Gew.-% Ethylen besteht, dadurch gekennzeichnet, daß das Harz einen Erweichungspunkt von 120 bis 180°C besitzt.

2. Folie nach Anspruch 1, bei der die Basisschicht 70 bis 90 Gew.-% des Polyolefins und 10 bis 30 Gew.-% des Harzes enthält.

3. Folie nach Anspruch 1 oder 2, bei der das Copolymer ein statistisches Copolymer ist.

4. Folie nach einem der vorangehenden Ansprüche, bei der das Polyolefin in der Basisschicht ein Polymer eines alpha-Monolefins mit 2 bis 4 Kohlenstoffatomen je Molekül, vorzugsweise Polypropylen ist.

5. Folie nach Anspruch 4, bei der das Polypropylen ein isotaktisches Polypropylen mit einer Dichte von 0,86 bis 0,92 g/ml gemessen bei 23°C gemäß ASTM D 1505 und einem Schmelzindex von 1 bis 15 g/10 min bestimmt nach ASTM D1238 (Bedingungen 230°C und 2,16 kg) ist.

6. Folie nach einem der vorangehenden Ansprüche, bei der das Harz hydriert ist.

7. Folie nach Anspruch 6, bei der das hydrierte Harz in der Basisschicht ein hydriertes Erdölharz ist.

8. Folie nach Anspruch 7, bei der das hydrierte Harz hergestellt worden ist, indem eine thermisch polymerisierte Dampfcrackdestillatfraktion oder eine katalytisch polymerisierte ungesättigte Kohlenwasserstofffraktion unter Verwendung eines Hydrierungskatalysators bei einer Temperatur von 200 bis 330°C hydriert worden ist.

9. Folie nach einem der vorangehenden Ansprüche, bei der das Harz einen Erweichungspunkt gemessen nach ASTM E28 von bis zu 150°C besitzt.

10. Folie nach einem der vorangehenden Ansprüche, bei der die Basisschicht 75 bis 85 Gew.-% Polyolefin und 15 bis 25 Gew.-% Harz enthält.

11. Folie nach einem der vorangehenden Ansprüche, bei der die Basisschicht auf jeder Oberfläche 1 bis 10 Gew.-%, bezogen auf das Gewicht der Basisschicht, der Folienschicht bestehend aus dem statistischen Copolymer aufweist.

12. Folie nach einem der vorangehenden Ansprüche, bei der das Copolymer ein statistisches Copolymer ist, das 94 bis 98 Gew.-% Propylen und 2 bis 6 Gew.-% Ethylen umfaßt.

13. Folie nach einem der vorangehenden Ansprüche, bei der das statistische Copolymer ein isotaktisches Propylen-Ethylen-Copolymer mit einer Dichte von 0,86 bis 0,92 g/ml gemessen bei 23°C gemäß ASTM D 1505 und einem Schmelzflußindex von 2 bis 15 g/10 min bestimmt gemäß ASTM D1238 (Bedingungen 230°C und 2,16 kg) ist.

14. Folie nach einem der vorangehenden Ansprüche, die biaxial orientiert ist.

15. Folie nach einem der vorangehenden Ansprüche, die 10 bis 60 µm dick ist und bei der die Dicke der oder jeder äußeren Folienschicht 0,05 bis 2,5 µm beträgt.

Revendications

1. Pellicule comportant une couche de base qui comprend 70 à 97% en poids d'une polyoléfine et 3 à 30% en poids d'une résine ayant un poids moléculaire inférieur à celui de la polyoléfine, ladite couche ayant sur au moins l'une de ses faces 1 à 20% en poids, sur la base du poids de la couche de base, d'une couche pelliculaire constituée d'un copolymère de 80 à 99% en poids de propylène et 1 à 20% en poids d'éthylène, caractérisée en ce que la résine a un point de ramollissement de 120 à 180°C.

2. Pellicule suivant la revendication 1, dans laquelle la couche de base comprend 70 à 90% en poids de la polyoléfine et 10 à 30% en poids de la résine.

3. Pellicule suivant la revendication 1 ou la revendication 2, dans laquelle le copolymère est un copolymère statistique.

4. Pellicule suivant l'une quelconque des revendications précédentes, dans laquelle la polypléfine de la couche de base est un polymère d'une mono-alpha-oléfine contenant 2 à 4 atomes de carbone par molécule, de préférence un polypropylène.

5. Pellicule suivant la revendication 4, dans laquelle le polypropylène est un polypropylène isotactique ayant une masse volumique de 0,86 à 0,92 g/ml, mesurée à 23°C conformément à la norme ASTM D 1505, et un indice d'écoulement à l'état fondu de 1 à 15 g/10 minutes tel que déterminé conformément à la norme ASTM D 1238 (conditions, 230°C et 2,16 kg).

6. Pellicule suivant l'une quelconque des revendications précédentes, dans laquelle la résine est hydrogénée.

7. Pellicule suivant la revendication 6, dans laquelle la résine hydrogénée dans la couche de base est une résine de pétrole hydrogénée.

8. Pellicule suivant la revendication 7, dans laquelle la résine hydrogénée a été préparée par hydrogénation en présence d'un catalyseur d'hydrogénation à une température de 200 à 330°C, d'une fraction de distillat craquée à la vapeur et polymérisée thermiquement ou d'une fraction hydrocarbonée non saturée polymérisée catalytiquement.

9. Pellicule suivant l'une quelconque des revendications précédentes, dans laquelle la résine a un point de ramollissement, mesuré d'après la norme ASTM E28, allant jusqu'à 150°C.

10. Pellicule suivant l'une quelconque des revendications précédentes, dans laquelle la couche de base comprend 75 à 85% en poids de polyoléfine et 15 à 25% en poids de résine.

11. Pellicule suivant l'une quelconque des revendications précédentes, dans laquelle la couche de base porte sur chaque face 1 à 10% en poids, sur la base du poids de la couche de base, de ladite couche pelliculaire constituée dudit copolymère statistique.

12. Pellicule suivant l'une quelconque des revendications précédentes, dans laquelle le copolymère est un copolymère statistique comprenant 94 à 98% en poids de propylène et 2 à 6% en poids d'éthylène.

13. Pellicule suivant l'une quelconque des revendications précédentes, dans laquelle le copolymère

statistique est un copolymère propylène-éthylène isotactique ayant une masse volumique de 0,86 à 0,92 g/ml, mesurée à 23°C conformément à la norme ASTM D 1505, et un indice d'écoulement à l'état fondu de 2 à 15 g/10 minutes, tel que déterminé conformément à la norme ASTM D1238 (conditions, 230°C et 2,16 kg).

14. Pellicule suivant l'une quelconque des revendications précédentes, qui est orientée biaxialement.

15. Pellicule suivant l'une quelconque des revendications précédentes, qui a une épaisseur de 10 à 60 µm et dans laquelle l'épaisseur de la couche ou de chaque couche pelliculaire externe est de 0,05 à 2,5 µm.

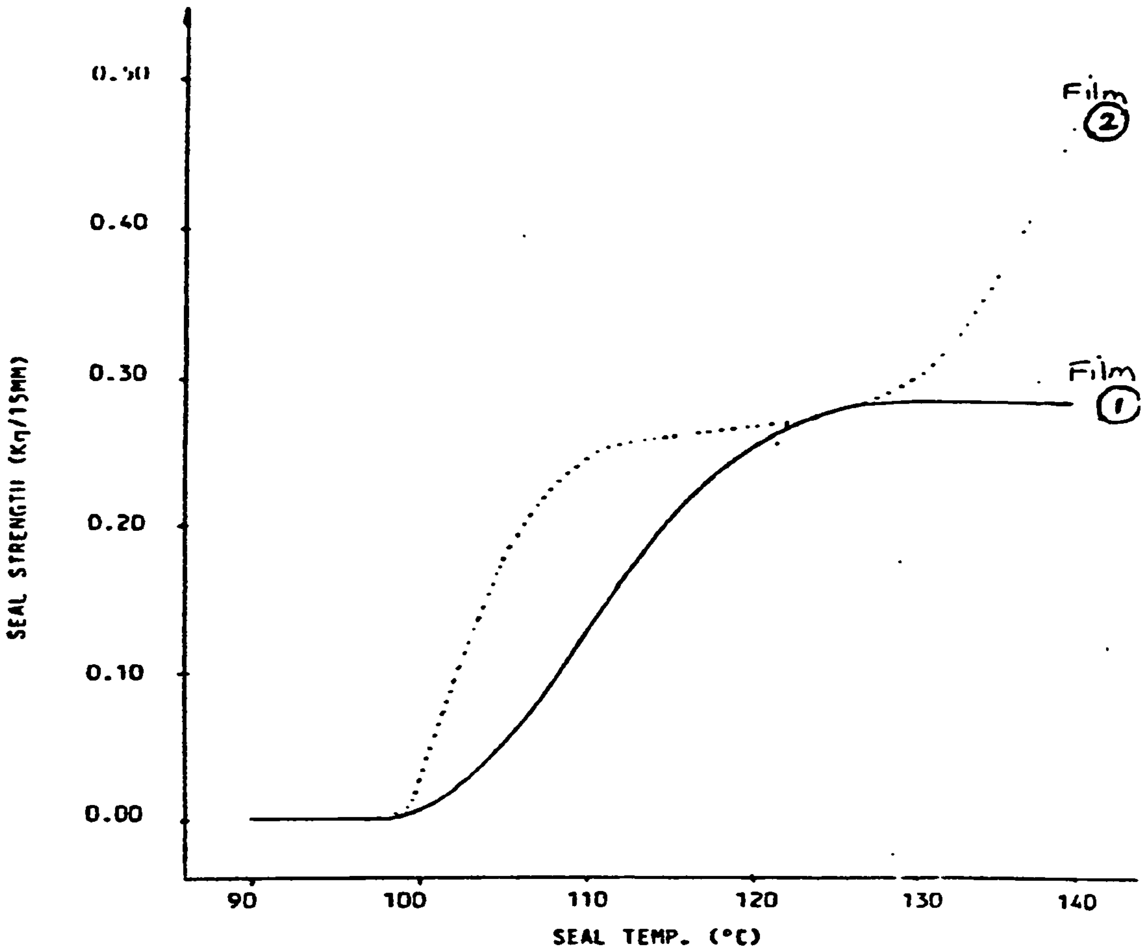

0.50
0.40
0.30
0.20
0.10
0.00
SEAL STRENGTH (Kg/15MM)
90
100
110
120
130
140
SEAL TEMP. (°C)
Film ②
Film ①

Fig 2

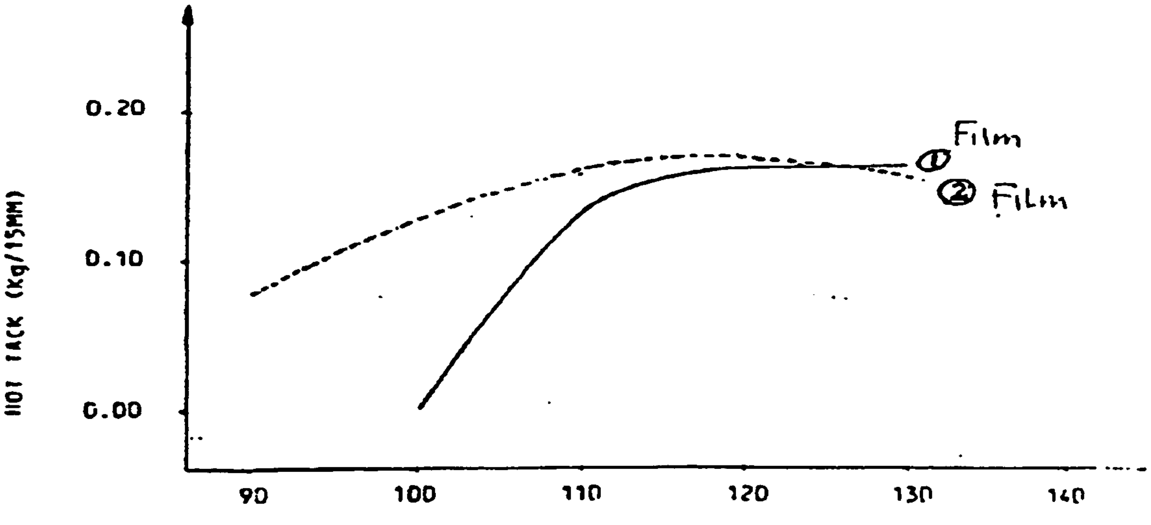

0.20
0.10
0.00
HOT TACK (Kg/15MM)
90
100
110
120
130
140
① Film
② Film

Fig 3

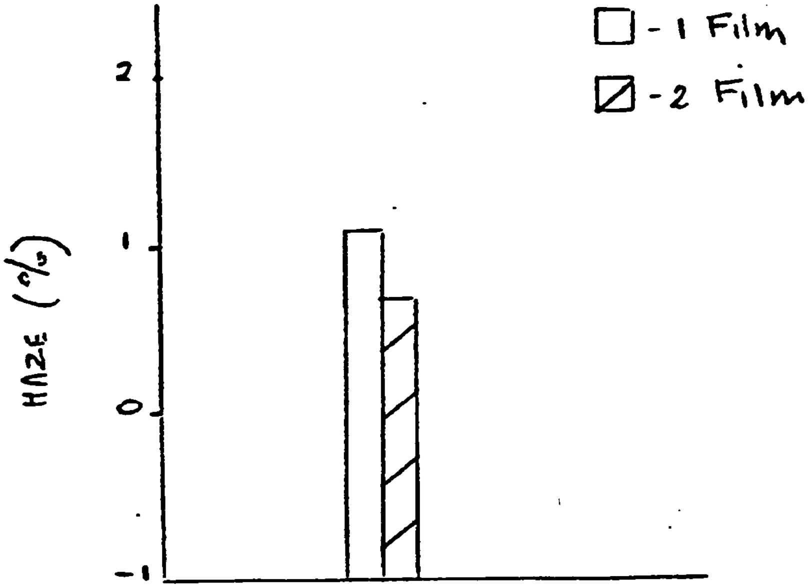


Fig 4

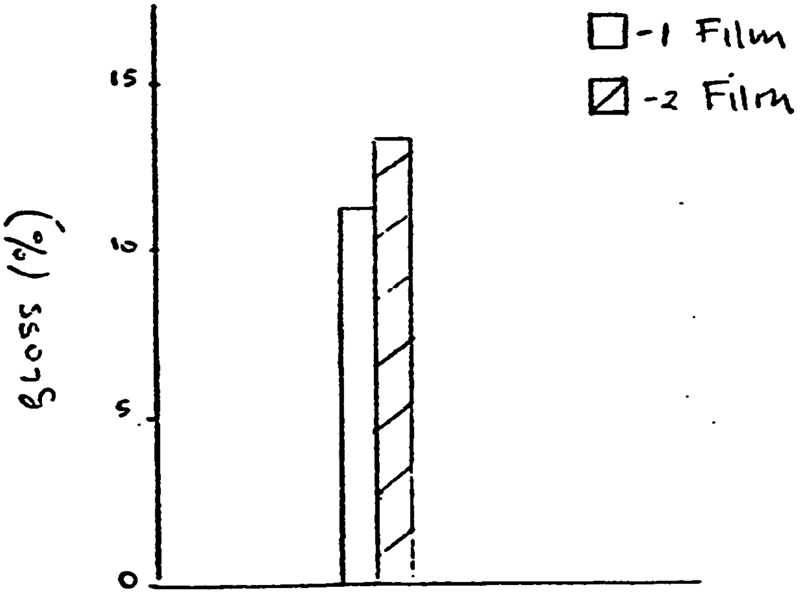


Fig 5

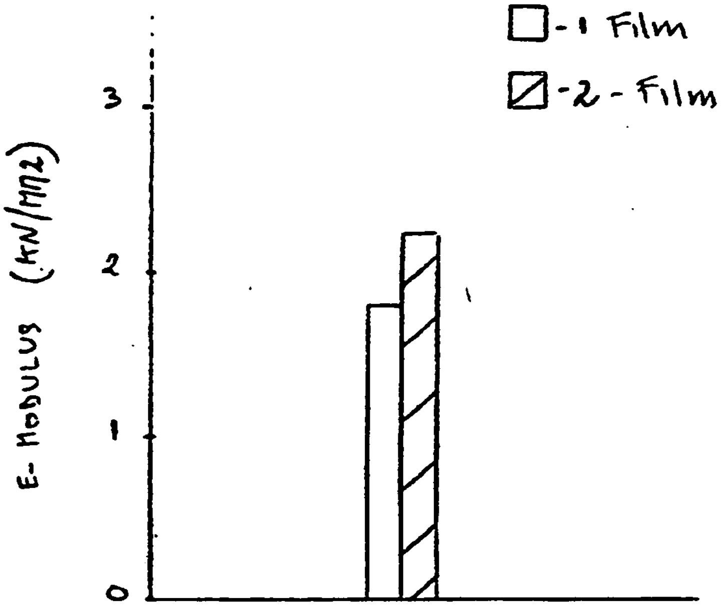
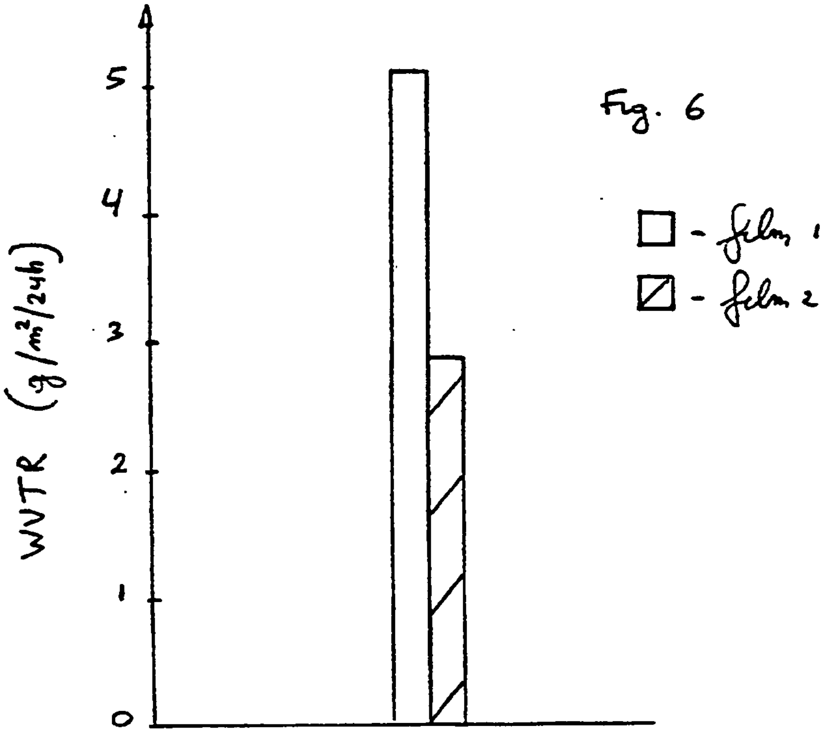


Fig. 6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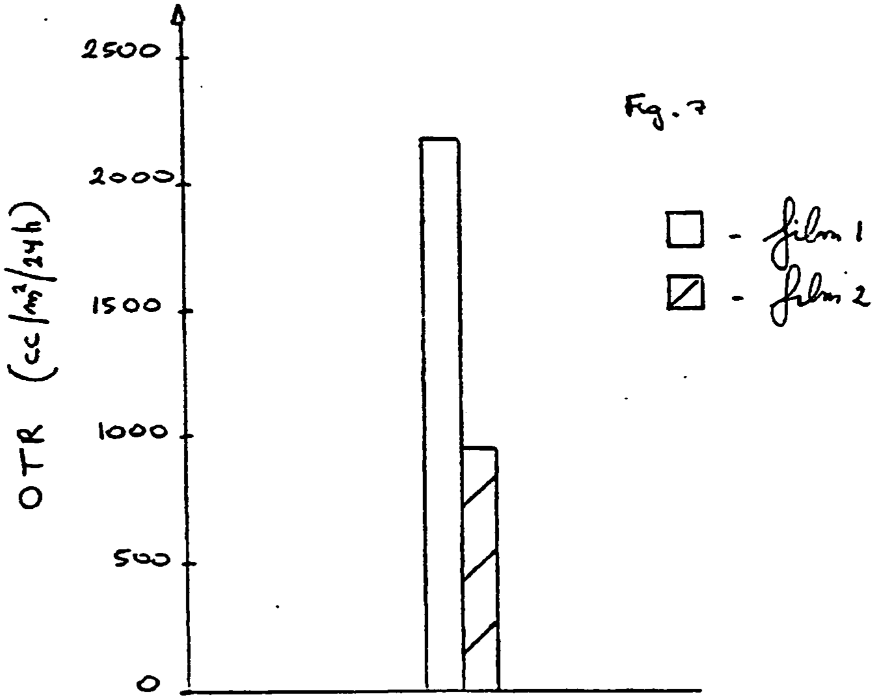
0
1
2
3
4
5
□ - film 1
▨ - film 2

Fig. 7


OTR (cc/m²/24h)
0
500
1000
1500
2000
2500
□ - film 1
▨ - film 2